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I, KIM MARSHALL, MANAGER PATENT OPERATIONS, hereby certify that the annexed is a true copy of the Provisional specification in connection with Application No. PP 3704 for a patent by NALCO AUSTRALIA PTY. LIMITED filed on 25 May 1998.

I further certify that the above application is now proceeding in the name of NALCO CHEMICAL COMPANY pursuant to the provisions of Section 113 of the Patents Act 1990.

I further certify that pursuant to the provisions of Section 38(1) of the Patents Act 1990 a complete specification was filed on 25 May 1999 and it is an associated application to Provisional Application No. PP 3704 and has been allocated No. 31255/99.



WITNESS my hand this Twenty-sixth  
day of July 1999

KIM MARSHALL  
MANAGER PATENT OPERATIONS

AUSTRALIA

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PATENTS ACT 1990  
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**PROVISIONAL SPECIFICATION**

***FOR THE INVENTION ENTITLED:-***

**"DEXTRAN, STARCH AND FLOCCULANT COMBINATION FOR  
IMPROVING RED MUD CLARIFICATION"**

The invention is described in the following statement:-

### **Field of the Invention**

The invention relates to a method for enhancing flocculation of red mud in the Bayer process and, more particularly, to the use of certain additives for increasing the settling rate of red mud and/or improving the clarity of the supernatant liquid.

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### **Background of the Invention**

In the Bayer process for the production of alumina, bauxite ore is pulverized, slurred in water, and then digested with caustic at elevated temperatures and pressures. The caustic solution dissolves oxides of aluminum, forming an aqueous sodium aluminate solution. The caustic-insoluble constituents of bauxite ore (referred to as "red mud") are then separated from the aqueous phase containing the dissolved sodium aluminate. Solid alumina trihydrate product is precipitated out of the solution and collected as product.

In more detail, the pulverized bauxite ore is fed to a slurry mixer where a water slurry is prepared. The slurry makeup water is typically spent liquor (described below) and added caustic. This bauxite ore slurry is then diluted and passed through a digester or a series of digesters where alumina is released from the ore as caustic-soluble sodium aluminate. The digested slurry is then cooled to about 110°C (about 230°F), typically employing a series of flash tanks wherein heat and condensate are recovered. The aluminate liquor leaving the flashing operation contains from about 1 to about 20 weight percent suspended solids, which solids consist of the insoluble residue that remains after, or is precipitated during, digestion. The coarser solid particles may be removed from the aluminate liquor with a "sand trap" cyclone. The finer solid particles are generally separated from the liquor first by settling and then by filtration, if necessary. The slurry

of aluminate liquor and the finer solids is normally first fed to the center well of a mud settler, or primary settler, where it is treated with a flocculant, and as the mud settles, clarified sodium aluminate solution, referred to as "green" or "pregnant" liquor, overflows a weir at the top. This overflow from the mud settling tank is passed to the subsequent process steps. If the aluminate liquor overflowing the settler contains an unacceptable concentration of suspended solids (at times from about 50 to about 500 mg of suspended solids per liter), it is then generally further clarified by filtration to give a filtrate with no more than about 10 mg suspended solids per liter of liquor. The treatment of the liquor collected after the primary settlement to remove any residual suspended solids before alumina trihydrate is recovered is referred to as a secondary clarification stage.

The clarified sodium aluminate liquor is seeded with alumina trihydrate crystals to induce precipitation of alumina in the form of alumina trihydrate,  $\text{Al}(\text{OH})_3$ . The alumina trihydrate particles or crystals are then separated from the concentrated caustic liquor, and the remaining liquid phase, the spent liquor, is returned to the initial digestion step and employed as a digestant after reconstitution with caustic.

In another section of the Bayer circuit, the settled solids of the primary settler ("red mud") are withdrawn from the bottom of the settler and passed through a countercurrent washing circuit for recovery of sodium aluminate and soda. The countercurrent washing circuit utilizes two or more washers which receive a mud washer feed slurry from either the settler underflow or other washer underflow, as well as any dilution liquor. As noted above, the red mud does not include any coarser particles removed prior to feeding the slurry to the primary or mud settler.

The at least partial separation of the red mud solids from the pregnant liquor at elevated temperatures by settling or by filtration is expedited by the use of a flocculant. This initial clarification of the pregnant liquor into a clarified liquor phase is referred to as the primary settler stage. Flocculating agents improve the separation of insolubles by increasing the rate at which the solids settle, by reducing the amount of residual solids suspended in the liquor, and by decreasing the amount of liquor in the settled solids phase. Flocculation performance is highly important in the primary settlement stages. Red muds are comprised chiefly of iron oxides (at least about 50 weight percent of the red mud solids), together with silicon oxides, calcium oxides, sodium alumino-silicates, titanium oxides and other materials, and commonly represent from about 5 to about 50 percent of the dry weight of the bauxite ore. Generally these muds are comprised of very fine particles, which hinder the desired rapid and clean separation of red mud particles from the solubilized alumina liquor. If the rate of separation is slow, output is materially diminished and overall process efficiency is impaired. If the separation is not clean, the resultant aluminate liquor will require a more extensive treatment to remove residual solids, and/or the alumina trihydrate recovered will contain levels of impurities that are undesirably high for many end-uses.

The polysaccharides starch and dextran were used early in red mud flocculation. For instance, U.S. Patent No. 3,085,853, April 16, 1963, Lesinski et al., uses native dextrans to increase the rate of sedimentation of finely divided solids in aqueous suspensions and thereby facilitate the separation of such solids. Later synthetic polymeric flocculants became more commonly employed for the Bayer process. U.S. Patent No. 3,390,959 issued July 2, 1968 to Sibert, uses acrylate homopolymers and

copolymers which contain not more than 20% of other ethylenically unsaturated polymerizable polar monomers for the Bayer process. Included in Sibert's polar comonomers are acrylamide and diethylvinylphosphonate, among others.

Diethylvinylphosphonate is the diethyl ester of vinylphosphonic acid, and can be hydrolyzed to the monoethyl ester in caustic solution.

U.S. Patent No. 3,397,953, August 20, 1968, Galvin et al., uses a blend of starch and polyacrylic acid on red mud suspensions, noting that polyacrylic acid alone is not suitable as a flocculating agent. The polyacrylic acids exemplified generally have molecular weights of less than 300,000. The flocculation and sedimentation activity of the blend is exemplified in the primary settler stage of a bauxite process. U.S. Patent No. 3,445,187, May 20, 1969, Sibert, uses synthetic acrylic acid polymer alone to enhance the rate of separation of red mud solids from the aqueous caustic solutions during secondary clarification steps. The synthetic polymer used contains at least about 80 weight percent of the acrylic acid mer unit, and has a molecular weight in excess of 50,000, and preferably in excess of 100,000. U.S. Patent No. 3,541,009, November 17, 1970, Arendt et al., uses a combination of causticized or modified starch, a water soluble polymer, and a caustic alkali to enhance the coagulation, sedimentation and/or filtration of aqueous suspensions of solids, including the settling of red mud from Bayer process liquor. The water soluble polymer is derived from at least one olefinically-unsaturated monomer and has a molecular weight in excess of 100,000.

U.S. Patent No. 3,681,012, August 1, 1972, Sibert, uses an acrylic acid polymer most preferably having a molecular weight of at least, 1,000,000, either alone or in combination with starch, for clarification of digested bauxite containing solubilized

alumina and red mud residues. U.S. Patent No. 4,767,540, August 30, 1988, Spitzer et al., uses a polymer that contains hydroxamic acid groups for the same purpose. U.S. Patent No. 5,008,089, April 16, 1991, Moody et al., uses a combination of dextran and synthetic anionic polymer for flocculating red mud in Bayer process liquors.

5 U.S. Patent No. 5,217,620, June 8, 1993, Mahoney et al., uses a combination of pullulan, lactan, rhamsan, or zooglan with a conventional water soluble anionic flocculant for red mud settling.

The synthetic flocculating agents employed for the settling or filtration of red mud are generally water soluble polymers of one or more ethylenically-unsaturated  
10 monomers, and have been used together, as noted above, with starch or dextran for aluminate liquor clarification. The synthetic flocculating agents are usually anionic, and the optimum anionic content of such polymer is usually related to the alkalinity of the liquor. In the washing circuit, the early wash liquors have the highest alkalinity and may require a more highly anionic polymer than the later wash liquors.

15 It is an object of the present invention to provide a more effective flocculation for separating red mud from the red mud-containing liquors, particularly preferably the primary settler liquor, of the Bayer process. It is a preferred object of the present invention to provide an improved method whereby the suspended solids retained in the supernatant phase after flocculation of the red mud-containing liquors, particularly the  
20 primary settler liquor, of the Bayer process are diminished. It is a further preferred object of the present invention to provide a more effective Bayer process wherein flocculation for separating red mud from the red mud-containing liquors, particularly the primary settler liquor, is improved by a more complete flocculation of the solids.

### Summary of the Invention

The claimed invention is a method for separating Bayer process red mud from a Bayer process liquor which includes:

5 contacting a Bayer process liquor containing red mud with, in combination, an effective amount of a water soluble synthetic flocculant, dextran and starch; and separating the flocculated red mud by a method selected from the group consisting of sedimentation, centrifugation and filtration.

The combination preferably contacts the slurry containing the red mud-suspended in Bayer process liquor, or a liquor slurry containing bauxite prior to or during  
10 digestion. The dextran, starch and flocculant combination can be added to the Bayer process liquor separately or together provided that in at least one point of the process a combination of all three components are present in the Bayer process liquor. If the three components are added separately, it is preferred to add the starch and polymer (separately or together) prior to the addition of the dextran. In preferred embodiments,  
15 the starch and polymer are added to the process upstream from the point of addition of the dextran.

Once the components of the combination are added, they are mixed sequentially with the Bayer process liquor and the red mud contained in the Bayer process liquor is removed by sedimentation, centrifugation or filtration.

20

### Description of the Invention

The present invention relates to a method which includes contacting a combination of a water soluble synthetic flocculant, dextran and starch to either a red mud slurry in



order to promote the flocculation of red mud, or with a digestion slurry to condition the resulting mud for improved flocculation.

Water-soluble synthetic flocculants which may be used with this invention include, but are not limited to acrylates, homopolymers of acrylic acid, copolymers of acrylic acid and acrylamide and copolymers of acrylic acid and acrylamide modified to contain  
5 a hydroxamic acid or acrylic acid moieties. Particularly preferred are ammonium acrylate polymers because of their replacement ratio and apparent synergy. The red mud thus treated may be separated from the liquor phase using a separator selected from the group consisting of settlers, thickeners, centrifuges and filters.

10 Preferably, the combination which contacts the Bayer process liquor is used in an amount of from about 0.01 to about 10 grams per liter of Bayer process liquor treated. The combination is more preferably used in an amount of from about 0.1 to about 2 grams per liter of liquor treated. The combination may contact the Bayer process liquor anywhere. For example the combination may contact the Bayer process liquor at a point  
15 selected from the group consisting of the primary settler feed, bauxite pretreatment, bauxite digestion and flash tanks. As stated above the dextran, starch and polymer may be added to the liquor separately or together. Preferably the starch and polymer are added together as one solution or separately as far back upstream from the addition of dextran as possible (the further back, the better for clarity reduction). For example the  
20 starch and polymer can be added as one solution or separately to a thickener feed line followed by addition of dextran to the feed line just prior to the feedwell or into the feedwell via sparges. Preferably the combination contacts the Bayer Process liquor in the primary settler feed.

The following examples are presented to describe preferred embodiments and utilities of the invention and are not meant to limit the invention unless otherwise stated in the claims appended hereto.

### **Brief Description of the Drawings**

5        Figure 1 is a graph comparing dosage of starch in grams per ton (gpt) to reduction in clarity.

### **Examples**

To evaluate the effectiveness of the combination, settling tests were completed in a waterbath with temperature maintained at 96°C. Eighteen (18) cylinders of identical  
10    mud/liquor characteristics were tested during one experiment.

High Molecular Weight Homopolymer Ammonium Acrylate (hereinafter referred to as Polymer A) with a molecular weight greater than 10 million and supplied by Nalco was diluted in spent liquor to a concentration of 1.5 gpl (0.15%) by introducing the neat polymer to the vortex produced by a cage stirrer at 800 RPM and mixing four five (5)  
15    minutes. Dextran (hereinafter referred to as Polymer B) produced by Pharmachem Corp USA and supplied by Weston Bioproducts as DEXTRAN 2P was diluted in lake water to a concentration of either 5 or 10 gpl (0.5 or 1.0%) by gentle mixing by shaking the bottle by hand. Starch was supplied as a 400 gpl (40%) solution and diluted with lakewater to 100 gpl (10%), and then further diluted with spent liquor to a final  
20    concentration of 20 gpl (2%) again by shaking the bottle by hand.

Polymer and Starch solutions were added together and the cylinders mixed using a gang plunger which allows six (6) cylinders to be tested at one time. After addition and

mixing of polymer and starch solutions the dextran solution was added and further mixing completed using the gang plunger.

Settling rate is presented in m/h and determined by measuring the time for flocculated mud particles to settle from 1000 ml to 600 ml in a 1000 ml cylinder.

- 5      Clarity was determined by decanting 250 ml of supernatant from the top of the settled cylinder after 30 minutes, adding 75 ml of 10N NaOH and boiling mixture to negate any precipitation of hydrate. After boiling, the liquor was cooled and passed through a turbidity meter and clarity determined and presented in NTU units.

TABLE 1

Cylinder	Plunges After Polymer/ Starch Addition	Plunges After Dextran Addition	Polymer Dose (ml)	Polymer Dose (gpt)	Starch Dose (ml)	Starch Dose (gpt)	Dextran Dose (ml)	Dextran Dose (gpt)	Settling Rate (m/h)	Clarity (NTU)	Reduction in Clarity (%)
1	20	10	4.0	150	0.0	0	0.4	100	2.9	220	0
2	20	10	4.0	150	0.5	250	0.4	100	3.4	215	2
3	20	10	4.0	150	1.0	500	0.4	100	4.1	210	5
4	20	10	4.0	150	1.5	750	0.4	100	4.1	200	9
5	20	10	4.0	150	2.0	1000	0.4	100	4.5	200	9
6	20	10	4.0	150	3.0	1500	0.4	100	4.9	155	30
7	20	10	4.0	150	0.0	0	0.8	200	3.8	245	0
8	20	10	4.0	150	0.5	250	0.8	200	4.4	225	8
9	20	10	4.0	150	1.0	500	0.8	200	4.4	215	12
10	20	10	4.0	150	1.5	750	0.8	200	4.5	210	14
11	20	10	4.0	150	2.0	1000	0.8	200	4.5	185	24
12	20	10	4.0	150	3.0	1500	0.8	200	5.1	145	41
13	20	10	4.0	150	0.0	0	1.6	400	4.5	215	0
14	20	10	4.0	150	0.5	250	1.6	400	4.6	205	5
15	20	10	4.0	150	1.0	500	1.6	400	5.4	160	26
16	20	10	4.0	150	1.5	750	1.6	400	5.6	140	35
17	20	10	4.0	150	2.0	1000	1.6	400	5.8	115	47
18	20	10	4.0	150	3.0	1500	1.6	400	6	95	56

TABLE 2

Cylinder	Plunges After Polymer/Starch Addition	Plunges After Dextran Addition	Polymer Dose (ml)	Polymer Dose (gpt)	Starch Dose (ml)	Starch Dose (gpt)	Dextran Dose (ml)	Dextran Dose (gpt)	Settling Rate (m/h)	Clarity (NTU)	Reduction in Clarity (%)
1	30	10	6.0	225	0.0	0	0	0	1.7	235	0
2	30	10	6.0	225	0.5	250	0	0	2.2	185	21
3	30	10	6.0	225	1.0	500	0	0	3.2	200	15
4	30	10	6.0	225	2.0	1000	0	0	3.6	215	9
5	30	10	6.0	225	3.0	1500	0	0	4.6	190	19
6	30	10	6.0	225	4.0	2000	0	0	4.6	160	32
7	30	10	6.0	225	0.0	0	1	250	3	210	0
8	30	10	6.0	225	0.5	250	1	250	3.7	200	5
9	30	10	6.0	225	1.0	500	1	250	4.5	200	5
10	30	10	6.0	225	2.0	1000	1	250	4.6	140	33
11	30	10	6.0	225	3.0	1500	1	250	6.4	110	48
12	30	10	6.0	225	4.0	2000	1	250	4.6	90	57
13	30	10	6.0	225	0.0	0	2	500	4.1	230	0
14	30	10	6.0	225	0.5	250	2	500	4.1	195	15
15	30	10	6.0	225	1.0	500	2	500	4.8	165	28
16	30	10	6.0	225	2.0	1000	2	500	4.5	135	41
17	30	10	6.0	225	3.0	1500	2	500	5.4	65	72
18	30	10	6.0	225	4.0	2000	2	500	5	50	78

The results are also shown in the attached Figure 1. It can be seen from the figure that including dextran and polymer in a starch flocculant combination resulted in a marked improvement in clarity.

This invention also relates to the use of the combination of a water soluble  
5 synthetic flocculant, dextran and starch for promoting coagulation or flocculation in other mineral slurries such as coal, kaolin, copper, precious metals, phosphate, taconite and refuse tailings obtained from these ores.

Changes can be made in the composition, operation and arrangement of the method of the present invention described herein without departing from the concept and  
10 scope of the invention as defined in the following claims.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:-

1. A method for separating Bayer process red mud from a Bayer process liquor which includes:  
contacting a Bayer process liquor containing red mud with, in combination, an  
5 effective amount of a water soluble synthetic flocculant, dextran and starch; and  
separating the flocculated red mud by a method selected from the group consisting of sedimentation, centrifugation and filtration.
2. The method of claim 1 wherein the water soluble synthetic flocculant, dextran and starch combination is used in an amount of from about 0.01 to about 10 grams per liter  
10 of liquor treated.
3. The method of claim 1 wherein the water soluble synthetic flocculant, dextran and starch combination is used in an amount of from about 0.1 to about 2 grams per liter of liquor treated.
4. The method of claim 1 wherein the water soluble synthetic flocculant, dextran and  
15 starch is added separately or together to the Bayer process liquor, the combination contacting the Bayer process liquor at one or more points selected from the group consisting of the primary settler feed, bauxite pretreatment, bauxite digestion, and the flash tanks.
5. The method of Claim 1, wherein the step of separating is carried out by a separator  
20 selected from the group consisting of settlers, thickeners, centrifuges and filters.
6. The method of Claim 1 wherein the flocculant is selected from the group consisting of homopolymers of acrylic acid, copolymers of acrylic acid and acrylamide, copolymers of acrylic acid and acrylamide modified to contain a hydroxamic acid

moiety and copolymers of acrylic acid and acrylamide modified to contain an acrylic acid moiety.

DATED this 25th Day of May 1998

NALCO AUSTRALIA PTY LIMITED

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### Abstract of the Invention

The claimed invention is a method for separating Bayer process red mud from a Bayer process liquor which comprises contacting a Bayer process liquor containing red mud with, in combination, an effective amount of a water soluble synthetic flocculant, 5 dextran and starch. The flocculant is contacted anywhere in the slurry containing the red mud suspended in Bayer process liquor, or in a liquor slurry containing bauxite prior to or during digestion. Once the flocculant combination is contacted it is mixed sequentially with the Bayer process liquor and the red mud contained in the Bayer process liquor is removed by sedimentation, centrifugation or filtration.

Figure 1

